

loses none of its activity. An experiment has been made with the object of reflecting the zinc action from glass. This did not succeed; whether this arose from the glass not being capable of effecting such a reflection, or whether a fortnight was not sufficient time to produce in this way a visible effect, is not known, but the experiment is being repeated. A photographic plate, suspended film upwards over a copal plate, was acted on round the edges in the way one would imagine a vapour to act. A similar experiment is being made over a zinc plate. The action of glass proves that there is at least a marked difference between the action exerted by metallic uranium and that by zinc and other metals.

It should be stated that it is only the most sensitive photographic plates which, without extremely long exposures, give the results described. The Mawson plate has generally been used in the foregoing experiments, but the Ilford special rapid plate acts equally well, and Edwards' isochromatic snap-shot plates are particularly sensitive to the action of the uranium salts. Lumière's extra rapid are not so sensitive as the Mawson and Ilford plates, and still less sensitive are the same firm's plates for yellow and green, and for red and yellow. Other sensitive plates have not been experimented with.

“On the Relative Behaviour of the H and K lines of the Spectrum of Calcium.” By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and Mrs. HUGGINS. Received May 27,—
Read June 17, 1897.

[PLATE 4.]

The remarkable relative behaviour of the lines in the spectra of certain substances as they appear at and near the sun's limb, and in the atmospheres of stars of different classes, has long been before our minds as a problem of great interest, which there is reason to believe is capable of solution by the methods of the laboratory, and on which we have worked from time to time for many years. Without waiting for the results of other researches which are in progress, we think that it is desirable to put on record some definite results on the behaviour of the lines of calcium, which appear to us to be conclusive, and of great importance in forming a correct interpretation of many solar and stellar phenomena.

As early as 1872, Professor Young from a few weeks' work at Sherman on the spectra of the chromosphere and of the prominences, was able to point out that “the selection of lines seems most capricious; one is taken and another is left, though belonging to the same element, of equal intensity, and close beside the first.” Especially he noticed that while the H and K lines of calcium are almost always

observable, the strong blue line as well as the other lines of this metal are very seldom seen. In his table of the chromospheric lines Professor Young gives for the frequency of this strong blue line the small number 3; while for the frequency of H and K, he gives respectively the high numbers 75 and 50.

From 1863, when I mapped the spectrum of calcium with a strong spark from metallic calcium* I have constantly used the lines of calcium as a comparison spectrum in stellar work. The experience was familiar to me that as the quantity of calcium salt on the electrodes became very small, H and K continued strong even when the other calcium lines had almost disappeared. The suggestion then occurred to me, that this behaviour of the lines might furnish a clue to the phenomena which take place near the sun's limb.

We were encouraged to use this experience as a guiding thought in the experiments about to be described, by the consideration that in the higher solar regions, where H and K appeared alone of the calcium lines, the density must be much less than at the lower level of the reversing layer. It seemed very probable that in the simple fact of difference of density, lay the true explanation of the modifications of the calcium spectrum as they are presented to us in solar and stellar phenomena.

The problem before us was, therefore, to find out by experiments in the laboratory, under what conditions the lines of calcium other than the lines H and K, and in particular the strong blue line at 4226·9, were so greatly enfeebled relatively to H and K, that they became quite insignificant, or even disappeared altogether from the spectrum, leaving the very simple spectrum of the two lines H and K, or nearly so.

Professor Lockyer states that:—"Some of the substances which have been investigated, including iron, calcium, and magnesium, have probably a definite spectrum, consisting of a few lines, which can only be completely produced at a temperature higher than any which is at present available in laboratory experiments." ('Roy. Soc. Proc.,' vol. 61, p. 205.)

In the case of calcium:—

"(4) A spectrum consisting of the two lines at 3703·18 and 3737·08 and the H and K lines, corresponding to a temperature higher than the average temperature of the spark, as before explained." (*Ibid.*, p. 161.)

Such a spectrum was not actually obtained, but experiments with a large intensity coil suggested that by a still greater increase of intensity of the spark such a simple spectrum might appear. The intensity of the strong blue line was reduced to one half of H and K. (*Ibid.*, Table, p. 162.)

* 'Phil. Trans.,' 1864, p. 139.

Kayser and Runge found 106 lines of the calcium spectrum to belong to the series of triplets; among the remaining lines they pointed out pairs with constant differences of wave-frequencies. Notably H and K, with a difference of wave-frequency of 222·9, and the more refrangible pair at 3737·08 and 3706·18, with a difference 223·1.

Messrs. Humphreys and Mohler in their experiments on the effect of pressure on the wave-lengths of metallic lines, found that in the case of calcium, the H and K lines were shifted only one-half as much as the blue line at 4226·9. We know far too little to justify us in forming any theoretical conclusions from this peculiarity of behaviour. Indeed there are no certain reasons why the lines of any substance should be equally shifted.

It is well known that calcium, in common with nearly all substances, gives a more complex spectrum under the conditions of the arc and spark than under those of a flame. Now in the Fraunhofer lines we have, as first shown by Kirchhoff and Bunsen, absorption spectra of the elements which correspond, speaking broadly, with those of the bright-lined spectra of the same substances as they are produced by the spark. In order, therefore, to study the modifications which the calcium undergoes in the higher regions of the chromosphere, in the prominences, and possibly in lower parts of the corona, as well as in the atmospheres of stars of different orders, it was clearly desirable that we should start with an ordinary spark spectrum. It was suggested to us strongly by the known rarer state of the gases in the regions above the photosphere, as well as by my long experience with the behaviour of calcium in comparison spectra that the modifications of the calcium spectrum which we were seeking, would be likely to show themselves under conditions of greatly reduced density of the calcium vapour.

Experiments.

For reasons which will be obvious later on, we elected to use throughout the experiments a spark of very small intensity.

1. The break of a 6-inch Apps coil was fixed at the position of smallest acting force of the spring. So much battery power only was employed as would be just sufficient to move the break. Under these conditions, when a jar was not in connection, the feeble spark would not pass when the distance between the points exceeded $1\frac{1}{4}$ inches.

2. In all the experiments a jar was intercalated.

3. The same length of exposure, a very short one of a second and a half, sufficient to bring out only the strongest lines of the spectrum, was used in each experiment.

4. Two sets of similar experiments were made; in one case with electrodes of platinum, and in the other with electrodes of iron. In the latter case the chief lines of iron were present with those of calcium.

Method adopted for reducing the Density of the Calcium Vapour.

(a) The spark was taken between electrodes of metallic calcium. It was assumed, as was confirmed by the appearance of the spark, that with metallic calcium for electrodes, the largest amount of calcium vapour would be present.

(b) The tips of the electrodes, iron or platinum, were slightly moistened with a strong solution of calcic chloride.

(c) The tips were slightly washed with pure water.

(d) The tips were again washed with pure water.

(e) The tips were then slightly moistened with a very weak solution, made by adding a drop of the strong solution to 2 ounces of water.

Our expectations were completely confirmed. Under the conditions (a) of greatest density of the calcium vapour, when metallic calcium was employed, the blue line was as strong and possessed the same diffuse character as H and K.

As the density of calcium was reduced, the lines were not found to be equally enfeebled, but, on the contrary, the blue line and the greater number of the lines were increasingly reduced in intensity relatively to H and K, until at last with the twice washed electrodes (d) the spectrum was simplified to the condition usually existing in the prominences, in which H and K only are present.

We now proceed to a more precise statement of the changes of relative intensity as they are presented in the photographs which accompany this paper.

Description of the Photographs on the Plate. (Plate 4.)

A. Photograph of the spark when both electrodes consist of metallic calcium. Here we have present doubtless the largest amount and greatest density of calcium vapour. The winged character of H and K, of the blue line, and of the pair more refrangible than H and K, is well seen, showing that this appearance comes out when the gas is dense. If the greater extension of the wings of H is allowed for, and the line H carefully distinguished from the fine lines close to it, it will be seen to possess very nearly the same strength, both as regards width and length, as the blue line at 4226.9. The strength of this blue line under this condition of density is about the same as that of the line at 3737, and rather greater than the line beyond at 3706.

B. Spark taken with one electrode only of metallic calcium, the other electrode being of platinum. In this case the effect of a smaller density of the calcium vapour is clearly shown in the greatly reduced wingedness of the lines. It will be remarked that the diminished density has had the greatest influence on the pair at 3737 and 3706; these lines are now much less strong than the blue line, which still holds its own, and remains about as strong as H and K. The lines of the more refrangible pair are no longer diffuse at the edges.

C. Spark taken between platinum electrodes moistened with a strong solution of calcium chloride. Here the effect of a smaller quantity of vapour begins to tell strongly upon the intensity of the blue line relatively to H and K. It may now be estimated at less than one-fourth of the intensity of H. At the same time, H and K have almost completely lost their diffuse character, and have become thinner and more defined.

D. The electrodes as left in the former experiment were slightly washed with pure water, leaving a trace only of calcium chloride. There is, as might be expected, an advance in the enfeeblement of the blue line and of the more refrangible pair, relatively to H and K.

E. The electrodes were again slightly washed with pure water, so that a still smaller trace of calcium chloride must have remained upon them. The enfeeblement of the blue line and of the pair has now become very great, while H and K, though thinner, remain strong.

F. The electrodes were once more washed with pure water, reducing still further the trace of calcium chloride which remained upon the platinum wires. The blue line has now practically disappeared, and the refrangible pair become very thin. The H and K lines have become thin and defined, as they usually present themselves in the prominences.

G. The electrodes remaining as they were left after the last experiment (F), the spark was taken upon a background consisting of a faint solar spectrum. The blue line has now completely disappeared, leaving H and K strong.

H. Once more the electrodes were washed, with the expectation of having removed completely the last remaining trace of calcium. To our surprise, when the photograph was developed, the lines H and K came out alone. The more refrangible pair had now faded out as well as the blue line. H and K were now thin, and extended but a short distance in the spectrum.

It must be remembered that the only condition which was varied during this set of experiments was the amount or density of the calcium vapour. The changes of relative intensity, and the modifications of the calcium spectrum produced thereby as shown in the

succession of photographs on the plate, correspond closely to the behaviour of calcium at different levels near the sun's limb, and in the atmospheres of stars of different orders. There can remain little doubt that the true interpretation of the changes in appearance of the calcium lines in the celestial bodies is to be found in the different states of density of the celestial gases from which the lines are emitted or by which they are absorbed.

A similar set of experiments was made with iron electrodes. Precisely similar results as to the relative enfeeblement of the lines, as with calcium chloride on platinum electrodes, were obtained. Of course the iron lines were also present. As might be anticipated, in consequence of the simultaneous presence of the iron vapour, the lines of calcium were thinner than when platinum was used.

Outside the range of wave-lengths which could be conveniently given on the plate, far on in the ultra-violet, there is a pair of strong lines which behave very much as H and K. It remains visible in photograph H, when the pair at 3737 and 3706 have disappeared. This pair is situated at 3158.98 and 3179.45.

It is desirable to point out again that all the photographs on the plate and the far ultra-violet lines, were obtained with a spark of quite unusually small intensity, which was purposely made as little hot as possible, in order to emphasize the important fact that the determining condition of the spectral changes under discussion is not one of increase of temperature.

In the modifications of the calcium spectrum arising from variations in the relative intensities of the lines which have been discussed in this paper, and which correspond to those observed in the celestial bodies, there does not appear to us any reason for assuming, much less any direct evidence in favour of, a true dissociation of calcium, that is, of its resolution into chemically different kinds of matter.

It would be remarkable if, by decomposition through increase of temperature, a large number of lines of a spectrum should become relatively enfeebled, and that as the result of decomposition a spectrum should become simpler, and not as analogy would suggest, more complex.

It is of importance to keep in mind that the recent chemical use of the word *dissociation* is not equivalent to true decomposition, *i.e.*, to a resolution of the original substance into two or more chemically different kinds of matter. It may, and does often mean not more than a different arrangement of the parts of the molecule, while those parts are all chemically matter of the same kind as the original molecule. As in the case of the resolution of a compound molecule of peroxide of nitrogen into two identical half molecules; or, in the separation of a molecule of elementary iodine into two half molecules or atoms of identical chemical

characters. Such dissociations are well known, and are not of infrequent occurrence, and may, indeed, take place in connection with some of the spectral changes of a substance observed under different conditions. On the other hand, a true decomposition of a chemical element, that is, a breaking up of the molecule into simpler and quite other kinds of matter, though a notion familiar to chemists since Prout's time, and regarded as theoretically possible, is, as yet, unknown as a matter of fact.

Conclusions.

These experiments seem to us to furnish an adequate and consistent explanation of the behaviour of the calcium lines at and near the sun's limb. Near the photosphere where the absorption mainly takes place, by which the dark lines of the solar spectrum are formed, there would be, we should expect, a much greater density of calcium vapour than at a higher level, and we find the Fraunhofer line at 4226.9 strong but much less broad than H and K. The recent photograph of the reversing layer shows that the broad shading of H and K is not produced there, but probably, as Prof. Jewell concludes from his measures, lower down where the gas is still denser, which is in agreement with photograph A on the plate.

Higher up in the chromosphere, in the prominences, and possibly in the lower coronal regions, the decrease of the density of the gases composing them must be rapid, and the temperature gradient as determined by expansion must be also rapid. We have clearly to do, in these regions, with calcium vapour in a rarer state, and except so far as the molecules may have carried up within themselves to some extent the higher heat of a lower level, or through imperfect transparency, the gases may have received heat from the sun's radiation, it must be at a much lower temperature than near the photosphere. Now, the changes of the calcium spectrum which take place in these regions, are those which correspond in our experiments to a very small amount of calcium vapour, and a spark of small intensity.

On account of the violent commotion which must exist through the strong convection currents at the sun's limb, we should not be surprised to find some calcium vapour, notwithstanding its greater density, carried high up together with the lighter substances such as hydrogen and helium. Our experiments show how strongly the H and K lines may come out when a trace only of calcium vapour is present, and so, it seems to us, offer a possible explanation of the great height at which these lines may be sometimes recognised. At no very great distance from the surface of the sun the gases must become too tenuous to give a visible spectrum; but it may well be that the brilliant radiations of even very rare calcium gas at H and K

may show in our instruments for some distance after the hydrogen and the other light matter associated with it, have become too subtle to furnish a spectrum that we can detect.

The relative behaviour of the lines of the calcium spectrum as they present themselves in the different orders of stellar spectra when interpreted by the terrestrial experiments described in this paper, will throw much light on many of the important questions which are still pending in celestial physics. In forming conclusions as to the state of the stellar atmospheres from the different densities which may be indicated by the modifications of the calcium spectrum, it must be borne in mind that, as I have said elsewhere:—

“The conditions of the radiating photosphere and those of the gases above it, on which the character of the spectrum of the star depends, will be determined not alone by temperature, but also by the force of gravity in these regions; this force will be fixed by the star’s mass and its stage of condensation, and will become greater as the star continues to condense.”*

It may be, though on this point we have as yet no sufficient data, that though the stars are built up of matter essentially similar to that of the sun, the proportion of the different elements is not the same in stars which have condensed in parts of the heavens widely distant from each other, or at epochs greatly separated in time.

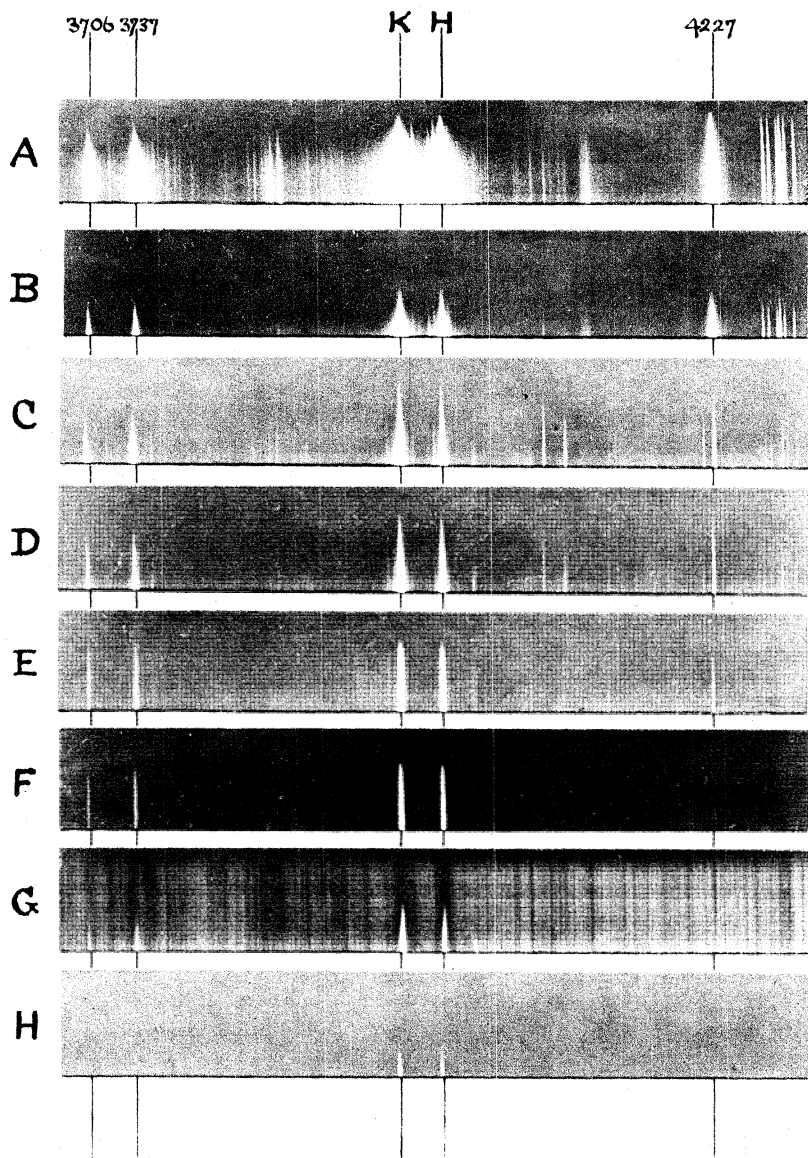
It does not seem desirable to discuss any of these questions at the present time, as we hope before long to offer some explanation of the, to some extent analogous, relative behaviour of the lines of some other substances as observed in the sun and stars.

[The following letter from our friend Professor Liveing, which he has given us permission to publish, contains an account of early experiments on the spectrum of calcium which not only support, by a different method of working, the conclusions of our paper, but also seem to suggest the possible occurrence of the line H without the line K. In our experiments both lines were always present, the line K being longer and stronger than H; conditions of the calcium lines which are in agreement with the photographs of the prominences taken by Hale and by Deslandres.

“I have been looking up some observations of Dewar’s and mine on the H and K lines of calcium made in 1879. We found that when we used, for the arc, carbon poles which had been heated for two days in chlorine to remove metals, the calcium lines were not at first visible in the arc, but after a time H was seen alone and not strong; after a further time, K was seen, and then other calcium lines came out. No doubt the calcium had been pretty well removed from the carbon rods to some depth, but not entirely from the

* Address, ‘Brit. Assoc. Report,’ 1891, p. 15.

SPARK SPECTRA SHEWING EFFECT OF DENSITY ON THE RELATIVE INTENSITIES OF THE LINES OF CALCIUM.



interior, so that as the carbon burnt away in the arc the calcium in the interior became manifest.

"Again, we found that when we used a perforated pole and passed a stream of hydrogen into the arc through it, H and K could be both entirely obliterated; but by then reducing the current of gas they gradually reappeared, and H always came out first and afterwards K; and H remained stronger than K, until they had both resumed their ordinary appearance. This observation was repeated several times.

"Both sets of observations, those with the purified carbon poles and those with the perforated pole, seem to me to confirm your conclusions.

"In the case of those with the perforated pole, the stream of hydrogen diluted the calcium vapour, and the degree of dilution was controlled by the rate at which the gas was introduced. The mass of gas passing was too small to reduce the temperature by any considerable amount, or even, I should think, to any sensible amount.

"We found also that metallic lithium, introduced into the arc, produced effects similar to those produced by hydrogen, that is, that it reduced very much the strength of the H and K lines. If more than a very minute piece of lithium were introduced, the arc was invariably broken, so that we did not notice the complete obliteration of H and K with the lithium.

"The reduction of the strength of H and K, in this case, I attribute to the dilution of the calcium vapour by that of lithium."
—June 25.]

"Further Observations of Enhanced Lines." By J. NORMAN LOCKYER, C.B., F.R.S. Received May 12,—Read June 17, 1897.

In a recent paper I gave an account of a series of experiments having for their object the determination of the lines which were enhanced in the spectra of iron, magnesium, and calcium, on passing from the arc to a high temperature spark, and I pointed out the presence of these lines in the spectra of the hotter stars and in the solar chromosphere.

The spectra of the following additional elements have since been investigated in a similar manner, and the enhanced lines have been tabulated and compared with chromospheric and stellar spectra.

